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(O/M) RATIO OF NUCLEAR FUEL

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# AIR-STABLE REFERENCE MATERIAL FOR MEASUREMENT OF THE OXYGEN-TO-METAL (O/M) RATIO OF NUCLEAR FUEL

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## ABSTRACT

As a reference material for the oxygen-to-metal (O/M) ratio of nuclear oxide fuel, pellets prepared by calcining powder blends of titanium suboxide and thorium oxide in hydrogen atmosphere have desirable features of controllable O/M-ratio values, long-term stability in air, absence of plutonium, and high resistance to fracture. Under the conditions of the O/M-ratio measurement method of heating at 800 to 900°C in an atmosphere of 6% hydrogen - 94% helium containing water vapor, the titanium suboxide oxidizes stoichiometrically to titanium dioxide. Pellets have been prepared having O/M-ratio values equivalent to values of 1.94 to 1.98 for 3/1 uranium/plutonium mixed-oxide fuel, and have been used effectively for calibration and quality-control surveillance of an automated, predictive-thermogravimetric analyzer being developed by the Hanford Engineering Development Laboratory.

## INTRODUCTION

The Hanford Engineering Development Laboratory is constructing a Secure Automated Fabrication facility for the production of mixed uranium-plutonium oxide fuel pellets (ref. 1). This facility will have a close-coupled chemical analysis system in which various specified components of the fuel will be determined at-line. The oxygen-to-metal (O/M) ratio is to be determined by a predictive thermogravimetric apparatus (ref. 2) having an objective elapsed time of 15 min. The analysis basis is dynamic measurement of the increasing weight of a fuel pellet having a hypostoichiometric O/M ratio as it is heated at 800 to 900°C in a 6% H<sub>2</sub> - 94% He atmosphere saturated with water vapor at 0°C to stoichiometric (U,Pu)O<sub>2</sub> (ref. 3,4). The total weight gain is predicted from the increasing weight gain.

The development of the apparatus required a reference material having features of (1) controllable O/M ratios equivalent to values of 1.94 to 1.98 for 3/1 uranium/plutonium mixed-oxide fuel, (2) long-term stability in air, (3) absence of plutonium, and (4) pellet form having high resistance to fracture. Pellets prepared by calcining powder blends of titanium suboxide and thorium dioxide meet all these features. This reference material, either in pellet or

hypostoichiometric oxide fuels are adjusted directly to the stoichiometric oxide by heating in a controlled atmosphere.

## EXPERIMENTS AND DISCUSSION

The required properties of a chemical compound for use as the reference material are a low-oxidation form that is stable in air and a high-oxidation form that is produced under the conditions of the O/M-ratio measurement method of heating at 800 to 900°C in the water-containing 6% H<sub>2</sub> - 94% He atmosphere. The selected mode of producing fracture-resistant pellets of the O/M reference material was (1) preparing a powder blend of a low-oxidation metal oxide, an inert metal oxide matrix, and an organic binder, (2) pressing pellets, and (3) calcining the pellets at 1600°C in a hydrogen atmosphere.

### Evaluation of Metal Oxides with Variable Oxidation States

Seven metal oxides, selected on the basis of the redox potential of the metallic element for reduction by hydrogen to a stable low-oxidation state, were investigated. The other required property of oxidation of the low-oxidation form to a high-oxidation form under the O/M-ratio measurement conditions was not considered predictable based on redox potentials.

Table I lists the experimental products of hydrogen reaction at 1600°C with the seven metal oxides followed by heating at 900°C in the water-containing 6% H<sub>2</sub> - 94% He atmosphere. Also listed are the products of subsequent heating at 1000°C in air.

TABLE I

Products of seven metal oxides heated sequentially under three conditions.

Initial Compound	Reaction with H <sub>2</sub> at 1600°C	Reaction with H <sub>2</sub> O-containing 6% H <sub>2</sub> -94% He at 900°C	Reaction with air at 1000°C
CeO <sub>2</sub>	Ce <sub>2</sub> O <sub>3</sub>	Not tested	Not tested
Cr <sub>2</sub> O <sub>3</sub>	None	None	None
Fe <sub>2</sub> O <sub>3</sub>	Fe metal	Partial oxidation	Not tested
MnO <sub>2</sub>	MnO	None	MnO <sub>3</sub>
Nb <sub>2</sub> O <sub>5</sub>	NbO <sub>2</sub>	Partial oxidation	Nb <sub>2</sub> O <sub>5</sub>
TiO <sub>2</sub>	Ti <sub>3</sub> O <sub>5</sub>	TiO <sub>2</sub>	None
V <sub>2</sub> O <sub>5</sub>	V <sub>2</sub> O <sub>3</sub>	None	V <sub>2</sub> O <sub>5</sub>

Only titanium oxide had the properties required for the reference material of reduction to a low-oxidation state upon heating with hydrogen and oxidation to a stable high-oxidation state under the O/M-ratio measurement conditions. It is therefore

was selected as the active component for the O/M-ratio reference material.

Although  $\text{CeO}_2$  reduced to  $\text{Ce}_2\text{O}_3$  with hydrogen at  $1600^\circ\text{C}$ , it is not practically useful as the component for an O/M-ratio reference material. The  $\text{Ce}_2\text{O}_3$  powder is unstable, in fact is pyrophoric, so that O/M-ratio reference material prepared with it would not be stable in air. Iron oxide is not suitable because the hydrogen reaction product of iron metal is not stable in air nor is it oxidized to a stable high-oxidation form under the O/M-ratio method conditions. Chromium, manganese, and vanadium oxides are not useful because the hydrogen-reaction low-oxidation forms do not oxidize to stable high-oxidation forms under the O/M-ratio method conditions.

#### Evaluation of Metal Oxides as the Inert Component

Three metal oxides,  $\text{Al}_2\text{O}_3$ ,  $\text{ThO}_2$ , and  $\text{UO}_2$ , selected on the basis that the products produced upon reaction with hydrogen at  $1600^\circ\text{C}$  would not oxidize under the O/M-ratio method conditions, were evaluated. Powder blends of each metal oxide,  $\text{Ti}_3\text{O}_5$ , and organic binder were prepared to have O/M ratios of 1.94 to 1.98 equivalent to mixed uranium-plutonium oxide, and pellets were pressed and calcined in hydrogen at  $1600^\circ\text{C}$ . These pellets were analyzed for their O/M ratios and their resistance to fracture was tested as described in a later section.

The pellets prepared using the  $\text{ThO}_2$  as the inert component had the highest long-term O/M-ratio stability in air and had excellent fracture resistance. Also their density, and hence weight for equal-size pellets, was close to that of uranium-plutonium mixed oxide fuel to serve as an effective reference material for the calibration of apparatus and methodology used for determining the O/M ratio of this fuel.

The pellets prepared using  $\text{UO}_2$ , which had an O/U ratio slightly greater than 2 had variations in their O/M-ratio values between and within batches that were unacceptably large. We observed porosity and density differences which could have affected the rates of hydrogen reduction of the hyperstoichiometric  $\text{UO}_2$  and the rates of oxidation of the hydrogen-reduced sintered pellets in the O/M-ratio measurement. The fracture resistance of these pellets was satisfactory.

The pellets prepared using  $\text{Al}_2\text{O}_3$  had long-term O/M-ratio stability in air; however, they were fragile so as not to withstand handling with the type of equipment being fabricated for the Secure Automated Fabrication facility. Also their density and weight for equal size pellets was low relative to that of uranium-plutonium mixed oxide pellets.

#### Fabrication of $\text{Ti}_3\text{O}_5$ - $\text{ThO}_2$ pellets

The  $\text{Ti}_3\text{O}_5$  was prepared by heating high-purity  $\text{TiO}_2$  powder in a tungsten crucible in a dry-hydrogen atmosphere at  $1625^\circ\text{C}$  for 3 h. The calcined product was

The  $\text{ThO}_2$  used was reactor-grade quality having an agglomerate structure,  $5.2 \text{ m}^2/\text{g}$  BET surface area,  $1.57 \text{ g/cm}^3$  bulk density, and  $7.7\text{-}\mu\text{m}$  average particle size. It was heated in air to remove volatile components, then passed through U. S. Standard No. 325 Sieve.

Weighed quantities of the  $\text{Ti}_3\text{O}_5$  and  $\text{ThO}_2$  to give O/M-ratio values of 1.94, 1.96, and 1.98, equivalent to 3/1 uranium/plutonium mixed oxide fuel, were roll-blended for 63 h in a glass bottle containing aluminum breaker bars and having an aluminum-foil liner in the lid. The masses of  $\text{Ti}_3\text{O}_5$  per gram of blend that give O/M-ratios of 1.94, 1.96, and 1.98 are 52, 35, and 18 mg.

The powder blends were pressed at 20 kpsi in a 6.09-mm steel die with double punches. A solution of stearic acid in acetone served as the die-wall lubricant.

The pellets, in a molybdenum V-block-boat assembly, were calcined in a dry-hydrogen atmosphere at  $1625^\circ\text{C}$  for 3 h. Their shrinkage was 15%.

#### Stability of Pellets and Reliability of the O/M-Ratios

The produced  $\text{Ti}_3\text{O}_5$  was evaluated for its stability, especially relative to moisture. The ultimate test was submersion of the powder for 24 h in water heated at  $80^\circ\text{C}$ . No change in appearance indicative of oxidation was observed. Afterwards the powder was dried in air to constant weight and weighed portions were ignited in air to produce  $\text{TiO}_2$ . The computed composition of the powder after its submersion in water still was  $\text{Ti}_3\text{O}_5$ .

The pellets prepared with O/M ratios of 1.94 to 1.98 have been stored in air having about 50% relative humidity for over 1 yr. Their O/M ratios have not changed.

The calcining of pellets has been done in batches of 50 to 100 and the O/M ratio was measured on four pellets from each batch. Table II summarizes the obtained O/M ratio results. The method measurement uncertainty, based on analysis of homogeneous powders, is 0.0015 standard deviation in absolute O/M-ratio values. The pooled standard deviation of the O/M-ratios, computed from the

TABLE II

Reliability of O/M-ratio in fabrication pellet batches.

O/M ratios, average $\pm$ standard deviation, in pellet batches having three $\text{Ti}_3\text{O}_5$ - $\text{ThO}_2$ compositions.		
18 mg $\text{Ti}_3\text{O}_5/\text{g}$	35 mg $\text{Ti}_3\text{O}_5/\text{g}$	52 mg $\text{Ti}_3\text{O}_5/\text{g}$
1.9798 $\pm$ 0.0021	1.9588 $\pm$ 0.0030	1.9390 $\pm$ 0.0008
1.9845 $\pm$ 0.0010	1.9595 $\pm$ 0.0006	1.9395 $\pm$ 0.0013
		1.9392 $\pm$ 0.0010
		1.9408 $\pm$ 0.0005

data given in Table II, is 0.0015, indicating that pellets are homogeneous within calcined batches.

### Fracture Resistance of Pellets

For application to the automated, predictive thermogravimetric apparatus, the pellets must resist fracture during operations with manipulators exerting a force of 28 g. Tests assessed resistance to compressive force and to fragmentation free-fall.

Compressive force was measured by placing a pellet on its curved surface between parallel, flat metal plates, then placing weights on top. Weight losses of pellets consistently were less than 0.02% at a maximum applied force of 1500 g. The pellets, therefore, resisted fracture at a force more than 50 times that exerted by manipulators having 28-g force and V-groove contacts.

In the free-fall test, pellets were dropped onto metal plates from a height of 25 cm, both vertically and at 45°, through glass tubes that had a diameter slightly larger than the pellets. Weight losses consistently were less than 0.02% for both the vertical fall where the pellets landed on their flat ends and for the 45° fall where they essentially landed with point contact.

### SUMMARY

A reference material for the measurement of the hypostoichiometric O/M ratio of nuclear fuel consists of pellets prepared from powder blends of  $Ti_3O_5$  and  $ThO_2$ . The powder also can be used. Features include controllable O/M ratios, greater than 1-yr stability in air, homogeneity, and high fracture resistance for the pellets.

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